Numerical integration of exchange energy in the two-dimensional Brillouin zone

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Abstract
A method is described for performing accurate numerical integration of the electronic exchange energy over polygonal regions in the two-dimensional Brillouin zone. It is illustrated by application to Bloch states constructed from Gaussian-type orbitals.

1. Introduction

Electronic structure studies on periodic systems typically involve electronic orbitals ψ of Bloch-wave type, of the form [1]

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{r} - \mathbf{R}), \qquad (1)$$

where ϕ is a localized orbital of some sort, the $\mathbf{R}$ sum is over the points of the direct-space lattice describing the translational symmetry of the system, and the wavevector $\mathbf{k}$ may be restricted to a unit cell of the system's reciprocal lattice centred about the origin (the Brillouin zone). Different $\mathbf{k}$ correspond to different orbitals, and in *ab initio* theory the system energy is described in terms of the integrals of energetic quantities, some of which are of the generic form

$$\int d\mathbf{k} \, d\mathbf{k}' \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \psi^*(\mathbf{k}, \mathbf{r}_1)\psi^*(\mathbf{k}', \mathbf{r}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi(\mathbf{k}'', \mathbf{r}_1)\psi(\mathbf{k}''', \mathbf{r}_2), \qquad (2)$$

where $\mathbf{k}''$ and $\mathbf{k}'''$ are, in either order, $\mathbf{k}$ and $\mathbf{k}'$, and the integrations of $\mathbf{k}$ and $\mathbf{k}'$ are over the occupied portion of the Brillouin zone.

Because the $\mathbf{R}$ sums resulting when equation (1) is substituted into equation (2) are slowly and conditionally convergent, it is most satisfactory to partition equation (2) between a direct-space and a reciprocal-space formulation with the aid of the Poisson summation formula [2–4]. The result is that both partitions become rapidly and absolutely convergent (with the former conditional convergence removed by an implicit choice of the long-range system boundary) [3].

The direct-space partition generally leads to quantities that cause no particular numerical difficulties when integrated over $\mathbf{k}$ and $\mathbf{k}'$. However, when Coulomb interactions are described in reciprocal space, a key quantity is the Fourier transform of the electrostatic potential, which is proportional to q^{-2}, where $\mathbf{q}$ is the transform variable. The values of $\mathbf{q}$ that occur have components in the periodic dimensions that are restricted to a discrete set of values. For the non-exchange parts of the electronic energy, these values are the non-zero points of the system's reciprocal lattice, and the factor q^{-2} generates no singularities [5]. In fact, for complete or partial Brillouin-zone integrations of the quantities referred to in this paragraph, satisfactory formulae have been given for quadratic approximations to both the integrand and the curves defining the region of integration [6–8].

In contrast, calculation of the exchange energy has historically been a source of difficulty. This is important because some features of the restricted Hartree–Fock (RHF) model, including the vanishing of the density of states at the Fermi level for situations of partial band occupancy [9, 10], cannot be reproduced without an accurate and explicit inclusion of the exchange contributions to the electronic energy [11, 12]. The problem arises because, for exchange involving orbitals of wavevectors $\mathbf{k}$ and $\mathbf{k}'$, the transform q^{-2} occurs with $\mathbf{q}$ values that include $\mathbf{q} = \mathbf{k} - \mathbf{k}' - \mathbf{K}$, where $\mathbf{K}$ ranges over all points of the reciprocal lattice, including zero. This creates a singularity in the integrand of equation (2) at $\mathbf{k} - \mathbf{k}' = \mathbf{K}$, certainly for $\mathbf{K} = 0$ and sometimes also for neighbouring $\mathbf{K}$ values. In spite of this singularity, the integral over $\mathbf{k}'$ (assuming it is performed first) converges, but its evaluation requires appropriate numerical techniques. Once the $\mathbf{k}'$ integral has been evaluated, the $\mathbf{k}$ integral presents no further difficulty.

The present study deals with systems possessing periodicity in two of the three dimensions. In that case, the reciprocal-space partition of the exchange energy, X_{r}, can be written

$$X_{\mathrm{r}} = \int \mathrm{d}\mathbf{k} \, X(\mathbf{k}), \tag{3}$$

where the $\mathbf{k}$ integration, and that of $\mathbf{k}'$ (see below), are over the occupied portion of the Brillouin zone. After integration of $\mathbf{q}$ in the nonperiodic dimension, $X(\mathbf{k})$ reduces, when Gaussian-type localized orbitals (GTOs) are used, to an expression of the general form [13–17]

$$X(\mathbf{k}) = \int \mathrm{d}\mathbf{k}' \sum_{\mathbf{K}} \frac{P(k'_x, k'_y)\mathrm{erfc}(\gamma |\mathbf{k} - \mathbf{k}' - \mathbf{K}|)}{|\mathbf{k} - \mathbf{k}' - \mathbf{K}|}, \tag{4}$$

where γ is a constant and P, which is a nonsingular function of its arguments (and also of the components of $\mathbf{k}$ and $\mathbf{K}$), is well represented locally by a low-order polynomial in k'_x and k'_y.

The subject of this paper is the evaluation by numerical integration of $X(\mathbf{k})$ as given in equation (4). A general approach that has been used in a variety of contexts involving momentum–space equations is to subtract from a singular integrand a term that leaves the remainder of the integrand nonsingular; a survey of these applications can be found in a recent paper by Ivanov and Mitroy [18]. The usual candidate for subtraction is a term that can be integrated analytically. However, in recent work on one-dimensionally periodic systems [11, 12, 19, 20], we found that the integrations over the nonperiodic dimensions led to incomplete Bessel functions [19–24] for which it was difficult to identify a subtractive term that would both remove the singularity and be integrable analytically. We proceeded instead by designing a quadrature scheme suitable for the singular form involved. We take a similar approach for the two-dimensionally periodic systems under discussion here.

Equation (4) exhibits a problem not encountered for one-dimensional periodicity, namely that the quantity $w = |\mathbf{k} - \mathbf{k}' - \mathbf{K}|$ introduces a branch-point singularity in both the numerator and the denominator of the integrand in that equation. To obtain an appropriate subtractive

contribution, we therefore make a substitution of the form $\text{erfc}(\gamma w) = 1 - \text{erf}(\gamma w)$, after which we recognize that $\text{erf}(\gamma w)/w$ is an analytic function of w^2 and thereby also a nonsingular function of the components of $\mathbf{k}'$. This brings equation (4) to the form

$$X(\mathbf{k}) = \int \mathrm{d}\mathbf{k}' \sum_{\mathbf{K}} \frac{P(k'_x, k'_y)}{|\mathbf{k} - \mathbf{k}' - \mathbf{K}|} - \int \mathrm{d}\mathbf{k}' \sum_{\mathbf{K}} \frac{P(k'_x, k'_y)\text{erf}(\gamma |\mathbf{k} - \mathbf{k}' - \mathbf{K}|)}{|\mathbf{k} - \mathbf{k}' - \mathbf{K}|}, \tag{5}$$

where the first integral has an integrand whose only singularity is from its denominator, while the second integral is completely nonsingular and can be evaluated using well-known methods.

In the next two sections of this paper we present a numerical method designed to handle the form

$$\int \mathrm{d}\mathbf{k}' \frac{P(k'_x, k'_y)}{|\mathbf{k} - \mathbf{k}' - \mathbf{K}|}, \tag{6}$$

where P is well approximated locally by a low-order polynomial in k'_x and k'_y. We note that the singularity illustrated by equation (6) is of a type that remains relevant even if localized orbitals other than GTOs were used. It would be desirable to be able to evaluate equation (6) numerically for regions with curved boundaries, as was done when the entire integrand is approximated by a polynomial [6–8]. An attempt to do so within the present context leads to elliptic integrals, so we have limited the analysis to regions with straight-line boundaries.

After completing the formal exposition, we provide an example illustrating its use. To facilitate the confirmation and use of the methods described here, we have placed on the Internet a Maple V program[4] that will generate the integration weights [25].

2. Integration of monomials

Letting x and y stand for the components of $\mathbf{k} - \mathbf{k}' - \mathbf{K}$, an integral of the form given in equation (6) can be cast in the form

$$I = \int_A \frac{f(x, y)}{\sqrt{x^2 + y^2}} \, \mathrm{d}x \, \mathrm{d}y, \tag{7}$$

where A indicates the region of integration. We assume that A can be approximated by a collection of polygonal cells, and seek formulae for an individual cell that will be exact when $f(x, y)$ is a low-degree polynomial in x and y. We note that the cell may or may not contain the point $x = y = 0$.

To develop an integration formula for a cell, we need values of I for the cell, with $f(x, y)$ successively chosen to be each monomial $x^p y^q$ of the polynomial approximation. One way to proceed is to reframe I as a line integral around the cell boundary. Using subscripts to indicate the monomial, we write

$$I_{pq} = \int_A \frac{x^p y^q}{\sqrt{x^2 + y^2}} \, \mathrm{d}x \, \mathrm{d}y = \int_C J_{pq}(x, y(x)) \, \mathrm{d}x, \tag{8}$$

where the curve C defines a clockwise path around A, $y(x)$ on the right side of equation (8) is the value of y for the point x on C, and $J_{pq}(x, y)$ is the indefinite integral

$$J_{pq}(x, y) = \int \frac{x^p y^q}{\sqrt{x^2 + y^2}} \, \mathrm{d}y. \tag{9}$$

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[4] Maple V is a product of Waterloo Maple Inc, Waterloo, ON, Canada.

For each monomial, we first evaluate $J_{pq}(x, y)$, then replace y by $ax + b$, where a and b are constants that will later be chosen to define particular cell boundary segments, and finally evaluate the indefinite integral of J_{pq}, which we denote K_{pq}:

$$K_{pq}(x, a, b) = \int J_{pq}(x, ax + b) \, \mathrm{d}x. \tag{10}$$

The curve C consists of a succession of line segments whose contributions to the line integral are to be summed. For the segment from (x_i, y_i) to (x_{i+1}, y_{i+1}), with $x_{i+1} \neq x_i$, we note that $a = (y_{i+1} - y_i)/(x_{i+1} - x_i)$, $b = y_i - ax_i$, and the contribution to I_{pq} is $K_{pq}(x_{i+1}, a, b) - K_{pq}(x_i, a, b)$. If $x_{i+1} = x_i$, there will be no contribution to I_{pq}.

The integrations needed to generate the $K_{pq}(x, a, b)$ are elementary, but somewhat tedious. With the aid of Maple, we obtained the following formulae for the six monomials with $p, q \leqslant 2$:

$$K_{00} = W + S, \tag{11}$$
$$K_{10} = \tfrac{1}{2}(bcR + xW - abcS), \tag{12}$$
$$K_{01} = \tfrac{1}{2}[(x + abc)R + bcS], \tag{13}$$
$$K_{20} = \tfrac{1}{6}[bc(x - 3abc)R + 2x^2W + b^2c^2(2a^2 - 1)S], \tag{14}$$
$$K_{11} = \tfrac{1}{6}[(2x^2 + abcx - b^2c + 3b^2c^2)R - 3ab^2c^2S], \tag{15}$$
$$K_{02} = \tfrac{1}{6}([a(x + abc)^2 + bc(x + 4abc)]R - x^2W - b^2c^2(a^2 - 2)S). \tag{16}$$

Here, $R = \sqrt{x^2 + (ax + b)^2}$, $S = bc^{1/2}\ln(c^{1/2}ab + c^{-1/2}x + R)$, $W = x\ln(ax + b + R)$, and $c = 1/(1 + a^2)$. Terms of any K_{pq} that are functions only of x (and not a or b) have been omitted because they will not give a net contribution for a closed path. The argument of the logarithm in S can vanish if $b = 0$ but, because the logarithm is multiplied by b, S in that case approaches zero as a limit. Similarly, the argument of the logarithm in W can vanish if $x = 0$, but W remains nonsingular.

We illustrate the use of the formulae in equations (11)–(16) by evaluating the integral $I_{pq} = \int x^p y^q (x^2 + y^2)^{-1/2} \, \mathrm{d}x \, \mathrm{d}y$ over a triangle with vertices at $(-2, -1)$, $(2, 1)$, and $(1, -2)$. A clockwise circuit of the triangle passes through these points in the order just given. For the segment from $(-2, -1)$ to $(2, 1)$, $a = 1/2$, $b = 0$; for $(2, 1)$ to $(1, -2)$, $a = 3$, $b = -5$; and for $(1, -2)$ to $(-2, -1)$, $a = -1/3$, $b = -5/3$. We therefore have

$$\begin{aligned} I_{pq} = {} & [K_{pq}(2, 1/2, 0) - K_{pq}(-2, 1/2, 0)] + [K_{pq}(1, 3, -5) - K_{p,q}(2, 3, -5)] \\ & + [K_{pq}(-2, -1/3, -5/3) - K_{pq}(1, -1/3, -5/3)]. \end{aligned} \tag{17}$$

The I_{pq} for this illustrative case are (to six significant figures): $I_{00} = 5.574\,30$, $I_{10} = 1.393\,57$, $I_{01} = -2.787\,15$, $I_{20} = 3.024\,70$, $I_{11} = 0$, and $I_{02} = 3.024\,70$.

3. Integration formulae

If, for a given cell, we have N monomial integrals, we can ordinarily expect to reproduce them exactly by an appropriate choice of weights for N integration points. We illustrate the weight determination for a triangular cell in which we have designated six points, equal in number to the monomials $x^p y^q$ with $0 \leqslant p + q \leqslant 2$. A reasonable choice of the six points is to use the three vertices of the triangle and the midpoints of its three sides. If we label the points (x_1, y_1)

through (x_6, y_6), the corresponding weights w_1 through w_6 must satisfy the matrix equation

$$
\begin{pmatrix}
1 & 1 & 1 & 1 & 1 & 1 \\
x_1 & x_2 & x_3 & x_4 & x_5 & x_6 \\
y_1 & y_2 & y_3 & y_4 & y_5 & y_6 \\
x_1^2 & x_2^2 & x_3^2 & x_4^2 & x_5^2 & x_6^2 \\
x_1 y_1 & x_2 y_2 & x_3 y_3 & x_4 y_4 & x_5 y_5 & x_6 y_6 \\
y_1^2 & y_2^2 & y_3^2 & y_4^2 & y_5^2 & y_6^2
\end{pmatrix}
\begin{pmatrix}
w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ w_6
\end{pmatrix}
=
\begin{pmatrix}
I_{00} \\ I_{10} \\ I_{01} \\ I_{20} \\ I_{11} \\ I_{02}
\end{pmatrix}. \qquad (18)
$$

Letting M, w, and I stand for the three matrices in equation (18), we may rewrite this equation in the form $\mathsf{M}\mathsf{w} = \mathsf{I}$, with solution $\mathsf{w} = \mathsf{M}^{-1}\mathsf{I}$. The locations on the triangle chosen for the six points ensure that the matrix M will be nonsingular, so that a nontrivial solution for w results.

Because the set of polynomials in x and y that is complete through any maximum degree will be closed under affine transformations, we note that, in the absence of the factor $1/\sqrt{x^2 + y^2}$, the corresponding set of I_{pq} would transform similarly to the monomials $x^p y^q$ under such transformations of its defining polygon. This observation corresponds to the known result that a conventional polynomial integration formula would have coefficients whose sum is the polygon's area, but otherwise are independent of the position or shape of the polygon [26]. However, in the present situation, the factor $1/\sqrt{x^2 + y^2}$ causes the I_{pq} not to transform like $x^p y^q$, with the result that the integration weights will depend on the position and shape of the defining polygon as well as on its area. There is, however, a useful scaling law: if the coordinate system is scaled uniformly by a factor s, the integration weights for the scaled polygon (in its scaled position) will be s times the original weights.

We close this section by illustrating the generation of weights for integrals of the form given in equation (7) over the triangle for which values of I_{pq} were listed at the end of the preceding section. For this case, the six integration points are $(-2, -1)$, $(2, 1)$, $(1, -2)$, $(\frac{3}{2}, -\frac{1}{2})$, $(-\frac{1}{2}, -\frac{3}{2})$, and $(0, 0)$. Equation (18) becomes

$$
\begin{pmatrix}
1 & 1 & 1 & 1 & 1 & 1 \\
-2 & 2 & 1 & 1.5 & -0.5 & 0 \\
-1 & 1 & -2 & -0.5 & -1.5 & 0 \\
4 & 4 & 1 & 2.25 & 0.25 & 0 \\
2 & 2 & -2 & -0.75 & 0.75 & 0 \\
1 & 1 & 4 & 0.25 & 2.25 & 0
\end{pmatrix}
\begin{pmatrix}
w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ w_6
\end{pmatrix}
=
\begin{pmatrix}
I_{00} \\ I_{10} \\ I_{01} \\ I_{20} \\ I_{11} \\ I_{02}
\end{pmatrix} \qquad (19)
$$

and its solution yields: $w_1 = -0.091\,8467$, $w_2 = -0.091\,8467$, $w_3 = -0.183\,6933$, $w_4 = 1.577\,2673$, $w_5 = 1.577\,2673$, and $w_6 = 2.787\,1480$.

4. Comprehensive example

To illustrate the use of the methods presented here, we consider a prototypical system consisting of a planar array of He atoms with nuclei at all cell origins in an infinite square lattice with lattice spacing a_0. The electron distribution will be constructed from a single normalized GTO of the form $\phi = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2)$ centred at each nucleus, and the electronic state will be a fully doubly occupied band, with wavevectors $\mathbf{k}$ in the xy plane whose components k_x and k_y (in units $2\pi/a_0$) are in the range $(-\frac{1}{2}, \frac{1}{2})$. To keep this example simple, we will work entirely in reciprocal space. After integrating the nonperiodic (z) coordinate, the exchange energy contribution corresponding to equation (4) can be written:

$$
X(\mathbf{k}) = -\frac{1}{2a_0} \int \mathrm{d}\mathbf{k}' \sum_{\mathbf{K}} S(\mathbf{k}, \mathbf{k} - \mathbf{k}' - \mathbf{K}) S(\mathbf{k}', -[\mathbf{k} - \mathbf{k}' - \mathbf{K}]) \frac{\mathrm{erfc}(\gamma|\mathbf{k} - \mathbf{k}' - \mathbf{K}|)}{|\mathbf{k} - \mathbf{k}' - \mathbf{K}|}. \qquad (20)
$$

The **K** summation is over an infinite square lattice of unit spacing (including **K** = 0), and the **k**' integration is over a unit square centred at the origin. S is a quantity which, for reference purposes, we specify more completely in an appendix; of importance now is that it is nonsingular and well approximated by polynomials in the components of **k**'. Finally, $\gamma = \pi/a_0\alpha^{1/2}$. Our concern here is the **k**' integration in equation (20).

Because the integrand of $X(\mathbf{k})$ is periodic (with period unity) in the components of **k**', and the present example has the simplifying feature of full, uniform band occupancy, we may make a change of variable from **k**' to $\overline{\mathbf{k}} = \mathbf{k} - \mathbf{k}'$, leading to

$$X(\mathbf{k}) = -\frac{1}{2a_0}\int d\overline{\mathbf{k}}\sum_{\mathbf{K}} S(\mathbf{k}, \overline{\mathbf{k}} - \mathbf{K})S(\mathbf{k} - \overline{\mathbf{k}}, \mathbf{K} - \overline{\mathbf{k}})\frac{\mathrm{erfc}(\gamma|\overline{\mathbf{k}} - \mathbf{K}|)}{|\overline{\mathbf{k}} - \mathbf{K}|}, \quad (21)$$

with the integration region for $\overline{\mathbf{k}}$ still a unit square centred at the origin. This transformation causes the singularity in the integrand of equation (21) to be limited to the summation term **K** = 0.

We now isolate the singularity by applying the technique illustrated in equation (5) to the **K** = 0 term of the sum, reaching

$$X(\mathbf{k}) = X_1(\mathbf{k}) + X_2(\mathbf{k}), \tag{22}$$

$$X_1(\mathbf{k}) = -\frac{1}{2a_0}\int d\overline{\mathbf{k}}\,\frac{S(\mathbf{k}, \overline{\mathbf{k}})S(\mathbf{k} - \overline{\mathbf{k}}, -\overline{\mathbf{k}})}{\overline{k}}, \tag{23}$$

$$X_2(\mathbf{k}) = -\frac{1}{2a_0}\int d\overline{\mathbf{k}}\left(-S(\mathbf{k}, \overline{\mathbf{k}})S(\mathbf{k} - \overline{\mathbf{k}}, -\overline{\mathbf{k}})\frac{\mathrm{erf}(\gamma\overline{k})}{\overline{k}}\right.$$

$$\left. + \sum_{\mathbf{K}\neq 0} S(\mathbf{k}, \overline{\mathbf{k}} - \mathbf{K})S(\mathbf{k} - \overline{\mathbf{k}}, \mathbf{K} - \overline{\mathbf{k}})\frac{\mathrm{erfc}(\gamma|\overline{\mathbf{k}} - \mathbf{K}|)}{|\overline{\mathbf{k}} - \mathbf{K}|}\right). \tag{24}$$

We will apply the integration formulae of this paper to $X_1(\mathbf{k})$; $X_2(\mathbf{k})$ can be evaluated by a straightforward application of Simpson's rule. When evaluating the integrand of $X_2(\mathbf{k})$ for $\overline{k} = 0$, the quantity $\mathrm{erf}(\gamma\overline{k})/\overline{k}$ must be replaced by its limit, $2\gamma/\pi^{1/2}$.

The first step in the evaluation of $X_1(\mathbf{k})$ is to prepare tables of integration weights. If the finest mesh to be used is, for some n, the set of points $\overline{k}_x = n_x/2n$, $\overline{k}_y = n_y/2n$, with n_x and n_y integers satisfying $-n \leqslant (n_x, n_y) \leqslant n$, we tile an integer mesh of these n_x and n_y with right triangles having sides of length two in the n_x and n_y directions, thereby causing the vertices and side midpoints of all triangles to lie on the integer mesh. We obtain integration weights for each of these triangles using the method discussed in an earlier section, and then combine and scale the weights as needed to build the desired overall integration schemes. As indicated in the introduction, Maple V programs for generating the weights have been placed on a publicly accessible web-site [25]. Weight tables for the $n = 8$ and 16 meshes are also available there.

We performed test calculations on a lattice with $a_0 = 2$ bohr and GTO exponent $\alpha = 0.868\,15$ bohr^{-2}. Our primary interest here is in values of $X_1(\mathbf{k})$ as defined in equation (23). Table 1 presents values of $X_1(\mathbf{k})$ for a variety of **k** (specified by the components k_x, k_y in units of $2\pi/a_0$), for integration meshes ranging from $n = 8$ to 64; the total number of points in an n-mesh is $4n^2$. The mesh for $n = 8$, with a total of 256 points, is already converged to four significant figures in almost the entire band; at $n = 16$, an additional two figures are obtained. The convergence and stability of the results are indicative that the formulae are error-free.

To further validate the numerical procedures, we combined $X_1(\mathbf{k})$ and $X_2(\mathbf{k})$ with the other quantities needed to make band energies $\epsilon(\mathbf{k})$. The detailed formulae used will be reported elsewhere [17]. These band energies were then compared with those obtained for the same system using the well-known *ab initio* program CRYSTAL [27]. The results, presented in table 2, are in agreement to within the probable accuracy of the CRYSTAL calculations.

Table 1. Exchange energy contributions $X_1(\mathbf{k})$, equation (23), for a planar array of He atoms (square lattice; lattice spacing 2.0 bohr; electronic wavefunction based on a single GTO with exponent $\alpha = 0.868\,15$ bohr^{-2}) at points k_x, k_y in the two-dimensional Brillouin zone as a function of integration mesh size n. An n-mesh places $4n^2$ points in the Brillouin zone.

k_x	k_y	$n = 8$	$n = 16$	$n = 32$	$n = 64$
0.	0.	$-3.896\,6577$	$-3.896\,3944$	$-3.896\,3794$	$-3.896\,3785$
0.2	0.	$-3.010\,8768$	$-3.010\,7480$	$-3.010\,7408$	$-3.010\,7404$
0.4	0.	$-1.796\,3702$	$-1.796\,3604$	$-1.796\,3598$	$-1.796\,3597$
0.5	0.	$-1.609\,3062$	$-1.609\,3754$	$-1.609\,3791$	$-1.609\,3793$
5/17	5/34	$-2.034\,9257$	$-2.034\,8978$	$-2.034\,8964$	$-2.034\,8963$
5/17	6/17	$-1.211\,7368$	$-1.211\,7431$	$-1.211\,7437$	$-1.211\,7437$
0.5	0.5	$-0.666\,8517$	$-0.666\,9811$	$-0.666\,9884$	$-0.666\,9888$

Table 2. Band energies for a planar array of He atoms (square lattice; lattice spacing 2.0 bohr; electronic wavefunction based on a single GTO with exponent $\alpha = 0.868\,15$ bohr^{-2}) at points k_x, k_y in the two-dimensional Brillouin zone as a function of integration mesh size n. An n-mesh places $4n^2$ points in the Brillouin zone.

k_x	k_y	$n = 8$	$n = 16$	$n = 32$	$n = 64$	CRYSTAL
0.	0.	$-1.362\,3156$	$-1.362\,1720$	$-1.362\,1639$	$-1.362\,1634$	-1.362
0.2	0.	$-1.138\,1626$	$-1.138\,0767$	$-1.138\,0719$	$-1.138\,0716$	-1.138
0.4	0.	$-0.542\,3444$	$-0.542\,3342$	$-0.542\,3336$	$-0.542\,3336$	-0.5421
0.5	0.	$-0.382\,5187$	$-0.382\,5974$	$-0.382\,6016$	$-0.382\,6018$	-0.3824
5/17	5/34	$-0.766\,2632$	$-0.766\,2377$	$-0.766\,2364$	$-0.766\,2364$	-0.7663
5/17	6/17	$-0.246\,1904$	$-0.246\,1993$	$-0.246\,2001$	$-0.246\,2001$	-0.2458
0.5	0.5	$+0.470\,3189$	$+0.470\,0124$	$+0.469\,9950$	$+0.469\,9940$	$+0.4690$

To assess the importance of the decomposition of the $\mathrm{erfc}(\gamma w)/w$ factor into $1/w -\mathrm{erf}(\gamma w)/w$, we performed a few calculations in which the method of this paper was applied to terms including $\mathrm{erfc}(\gamma w)/w$ instead of applying it only to the $1/w$ part of its decomposition. The results were quite poor; the $n = 32$ mesh only yielded three significant figures for X_1. This is indicative of the fact that, even though the remaining branch-point singularity does not make the integrand infinite, it nevertheless has a substantial effect on the numerical integration process and cannot be neglected.

5. Possible extensions

It would be desirable to generalize the method presented here to treat regions of the Brillouin zone delineated by curved boundaries, as was done [6–8] for the nonexchange energy contributions. As pointed out earlier, we did not do so here, because that would cause the formulae in equations (11)–(17) to contain incomplete elliptic integrals. In principle, there is no fundamental reason why such a course could not be pursued, and it could form the basis of a future investigation.

Another possible direction for generalization would be to systems that are periodic in all three spatial dimensions. In some ways, the 3D periodic problem is similar to that encountered with one-dimensional periodicity; the basic quantity to be integrated has a pole, but not a branch point at $\mathbf{k} - \mathbf{k}' - \mathbf{K} = 0$, and expressions appropriate to that particular situation would need to be developed. The three-dimensional integration region could be divided into tetrahedra in such a way that causes lattice points to be at all vertices and edge midpoints of each tetrahedron. This would lead to a requirement for formulae analagous to equations (11)–(17) for all monomials

$x^p y^q z^r$ of combined degree $\leqslant 2$; to develop the details and to document the effectiveness of the approach would take us considerably beyond the scope of the present report.

Acknowledgments

Appendix

The quantity $S(\mathbf{k}, \mathbf{q})$ can be computed in a number of different ways. The formula given here is intended mainly to secure its definition:

$$S(\mathbf{k}, \mathbf{q}) = \sum_{\mathbf{K}} e^{2\pi i \mathbf{K} \cdot (\mathbf{k} + \mathbf{q}/2) - \pi^2 K^2 / 2\gamma^2}. \tag{25}$$

The $\mathbf{K}$ summation is over an infinite square lattice of unit spacing (including $\mathbf{K} = 0$), and $\mathbf{k}$ and $\mathbf{q}$ are in the dimensionless units used in the main text.

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